CHARGE TRANSFER SPECTRA OF TRIMETHYLSILYL SUBSTITUTED AROMATIC COMPOUNDS

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Introduction

The charge transfer complexes (CT complexes or donor-acceptor complexes) can be recognized by the appearance of a new absorption band in their spectra in the near UV or visible region, this band is not characteristic of the spectrum of either the electron donor (D) or the electron acceptor (A). If aromatic systems act as donors and they form CT complexes of (π, π) type with the applied acceptor, the energy of the charge transfer absorption can be obtained according to DEWAR and al. [1, 2] by the following equation:

$$h \cdot \nu_{\mathrm{CT}} = E_{\mathrm{m+1(A)}} - E_{\mathrm{m(D)}} + P$$

where $E_{\mathrm{(m+1)A}}$ and $E_{\mathrm{(m)D}}$ are the energies of the first unoccupied molecular level of the acceptor and the last occupied molecular level of the donor molecule, respectively, P is an energy contribution taking the perturbation of the donor and acceptor into account.

WENTHWORTH and al. [3] found a linear relationship between the energy of the charge transfer band of lower energy and the ionization potential of the donor:

$$h\nu_{\mathrm{CT}} = f(I_{\mathrm{D}}) = a\ I_{\mathrm{D}} + b \qquad (I_{\mathrm{D}} > 6\ \mathrm{eV})$$

The latter linear relation is generally used in practice, the value of constants a and b, however, vary within a rather wide interval.

The investigation of donor-acceptor complexes of organosilicon compounds was first carried out by BOCK and ALT [4], and they declared that the inductive polarization caused by the R_3Si group was partly compensated by $Si \leftarrow C_\pi$ back-donation. In the interpretation of the spectra of complexes generated from trimethylsilylbenzene and tert-butylbenzene by tetracyanoethylene (TCNE) they considered the effect of $d-\pi$ interaction. The same authors analyzed the spectra of CT complexes between a number of mono-, di-, tri-, tetrasubstituted organosilicon benzene derivatives and TCNE [5], and found correlation between the measured ionization potentials of the organosilicon com-

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*Research Institute for the Plastics Industry, Budapest pounds and the frequency of the charge transfer absorptions observed at higher wavelengths. On the basis of their results the existence of $(p-d)\pi$ interaction in ground state was concluded.

Investigating the CT complexes of TCNE and pentamethyldisilanyl substituted benzene and naphthalene, Sakurai and Kira [6] referred to $\sigma-\pi$ interaction between the Si—Si bond and the aromatic π electron cloud, their assumption was supported quantumchemically by perturbation calculation.

Evans and al. [7] recorded the CT spectra of some trimethylsilyl substituted naphthalene derivatives. The observed hypsochromic shift of the charge transfer absorption bands in comparison with the analogous carbon compounds was interpreted by the formation of $(p-d)\pi$ bond in ground state.

The CT complexes of substituted silylacenaphthenes with TCNE were investigated by Ponec and al. [8] in CH_2Cl_2 solution. They explained the electron withdrawing property of silyl substituents by hyperconjugative mechanism.

Experimental

TCNE was used as acceptor for the charge transfer complexes of (π, π)-type. This compound was preferred since it had no absorption in the wavelength range of CT bands and the experiments on the CT complexes of organosilicon compounds have been carried out with this compound [4—8]. For the same reasons, CH_2Cl_2 was used as solvent.

The donor-acceptor complexes were always formed with donor excess to make the Benesi—Hildebrand method of graphic evaluation [9] applicable. The pure complexes were not prepared, only their solutions were studied. The colour of the solutions was orange or greenish-yellow for benzene derivatives, blue gray or reddish-brown for naphthalene derivatives, violet for phenanthrene compounds and green or greenish-brown in the case of anthracene derivatives.

The spectra of the complexes were recorded by a Unicam SP-700 instrument at 25 °C. Fig. 1 and Fig. 2 show the spectra of charge transfer complexes of benzene and naphthalene derivatives, respectively.

In the case of benzene compounds a typical asymmetric charge transfer band can be observed, which is more flat on the blue side, thus for wavenumbers corresponding to $\varepsilon_{\max}/2$ it is true that

$$(\tilde{\nu}_{\max} - \tilde{\nu}_r) < (\tilde{\nu}_b - \tilde{\nu}_{\max})$$

and generally [10]:

$$\tilde{\nu}_b - \tilde{\nu}_r \simeq 2{,}4(\tilde{\nu}_{\max} - \tilde{\nu}_r)$$

where subscripts b and r refer to the blue and red side of the band, respectively.

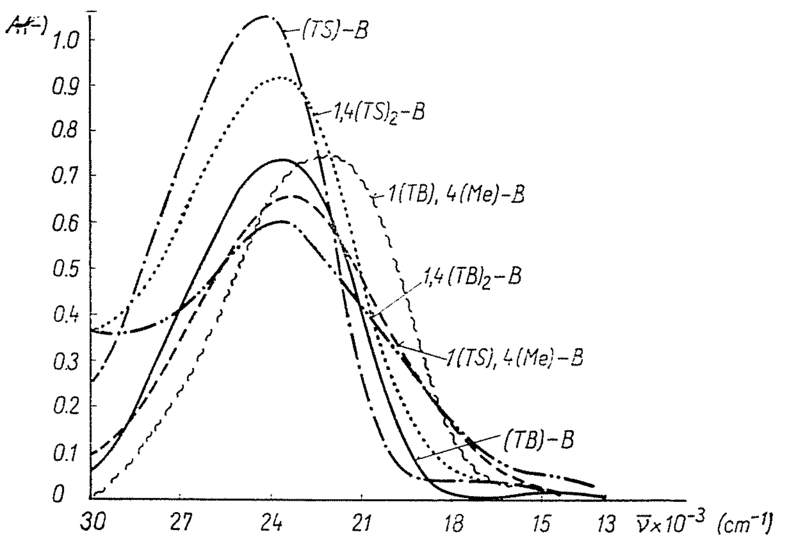

Fig. 1. Charge transfer absorption bands for benzene derivatives (B: benzene, TB: tertiary butyl substituent, TS: trimethylsilyl substituent, Me: methyl substituent)

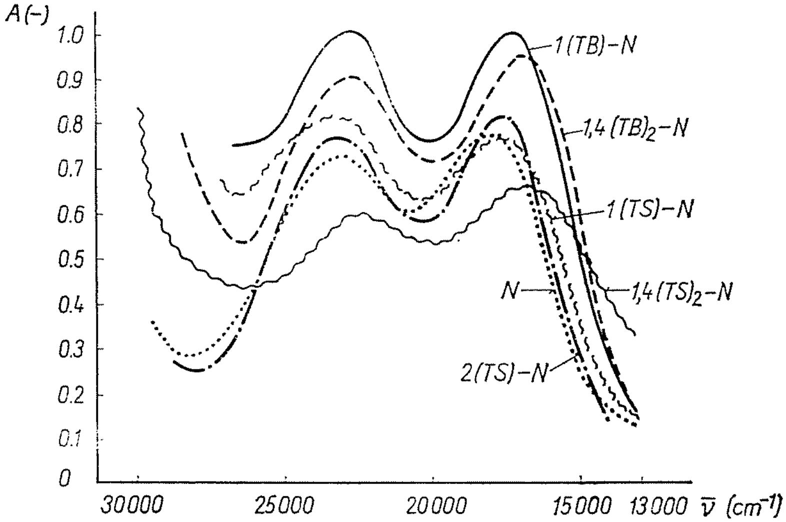

Fig. 2. Charge transfer absorption bands for naphthalene derivatives (N: naphthalene, TB. tertiary butyl, TS: trimethylsilyl)

It is seen from the figures that the CT bands of carbon compounds are shifted toward the lower wavenumbers in comparison to those of the organosilicon compounds.

The charge transfer bands of the investigated anthracene compounds are of smaller intensity, and the charge transfer absorption band of higher energy (CT II) overlaps with the UV absorption band of the donor.

In the case of phenanthrene compounds the displacements of the band is of a very low degree. The evaluation of the extremely intensive charge transfer band is impeded by the superposition of bands.

According to the experimental findings the energy of the charge transfer absorption decreases in the following order:

unsubstituted aromatic compound > trimethylsilyl substituted derivative > tert-butyl substituted derivative.

Results and discussion

The spectral data of the investigated charge transfer complexes are summarized in Table 1, the data taken from the literature are also presented.

Table 1

Data of charge transfer bands

Compounds	(in kK) CT (I)	(in kK) CT (II)	CT (I)	CT (II)
B (benzene)	26,05^{a}; 26,00^{b}		2850	
TS-B	24,36; 24,65^{a}; 24,50^{b}		770	
TB-B	23,98; 24,00^{a,b}		2070	
1(TS),4(Me)-B	23,04; 23,50^{b}		870	
1(TB),4(Me)-B	21,98		1820	
1,4(TS)$_2$-B	23,67; 23,90^{a}		410	
1,4(TB)$_2$-B	23,70; 23,90^{a}		1930	
N(naphthalene)	18,05; 18,20^{c}	23,15; 23,30^{c}	1300; 1200^{c}	1250; 1100^{c}
1(TS)-N	17,51; 17,50^{c}	22,99; 23,00^{c}	1200; 1220^{c}	1000; 1120^{c}
1(TB)-N	17,18; 16,90^{c}	22,88; 22,80^{c}	760; 715^{c}	820; 370^{c}
2(TS)-N	17,57; 17,80^{c}	22,68; 22,60^{c}	900; 400^{c}	760; 233^{c}
1,4(TS)$_2$-N	17,21; 17,00^{c}	22,52; 22,40^{c}	300; 81^{c}	230; 89^{c}
1,4(TB)$_2$-N	16,58; 16,00^{c}	22,52; 22,50^{c}	680; 47^{c}	590; 53^{c}
A (anthracene)	14,71; 13,50^{d}	21,79; 21,50^{d}	—	
9,10(TS)$_2$-A	14,49	21,60	—	
9,10(TB)$_2$-A	14,08	21,28		
P (phenanthrene)	18,52; 18,52^{e}		772	
9(TS)-P	18,50		716	
9(TB)-P	18,32		1180	
4,10(TS)$_2$-P	18,48		720	
4,10(TB)$_2$-P	18,21		1000	

Designation: a) ref. [5]; b) Ponec, R., Chvalovsky, V.: Coll. Czech. Commun. **39**, 1313 (1974); c) ref. [7]; d) Briegleb, C.: Electronen-Donator-Acceptor-Komplexe. Springer Verlag, Berlin, 1961; e) Kuban, V., Jamak, J.: Chem. Listy, **63**, 639 (1969)

In the case of substituted benzenes the asymmetric shape of the charge transfer bands can be attributed to the effect of the substituent which changes the symmetry conditions and lifts the degeneracy of the energy levels of the unsubstituted compound. The overlapping of the CT I and CT II bands, however, is maintained. For the appearance of two distinguished bands, fairly large energy difference between the symmetric and antisymmetric molecular levels of benzene is necessary. Another requirement is the comparable magnitude of the molar extinction coefficients for the two bands.

In the case of benzene and phenanthrene compounds the splitting of CT bands was not observed (Table 1). Bock and Alt pointed out [5] that the extinction coefficient of the CT I band of organosilicon benzene compounds is much smaller than that of the CT II band.

The CT I band (at longer wavelengths) and the CT II band (at shorter wavelengths) of naphthalene derivatives are sharply distinguished. The $-SiMe_3$ substituted compounds show a hypsochromic shift in comparison to the $-CMe_3$ substituted derivatives and a bathochromic shift compared to the unsubstituted compound.

In the case of anthracene derivatives the CT II band overlaps with the ultraviolet *p*-band of the donor, for this reason the data in Table 1 are the results of graphic evaluation. The CT spectra of phenanthrene derivatives are also indicating band overlappings. Therefore there are no essential differences between the CT data of phenanthrene and its $-SiMe_3$ substituted derivatives. The bathochromic displacement for the $-CMe_3$ substituted derivatives is somewhat more significant in comparison with the spectrum of CT complex of phenanthrene.

In general, substituent $-CMe_3$ decreases the absorption frequency in respect to the unsubstituted aromatic compound, the effect of $-SiMe_3$ group is also indicated by a red shift, but the displacement of the absorption bands is of smaller degree than for the $-CMe_3$ substituted compounds (Fig. 3).

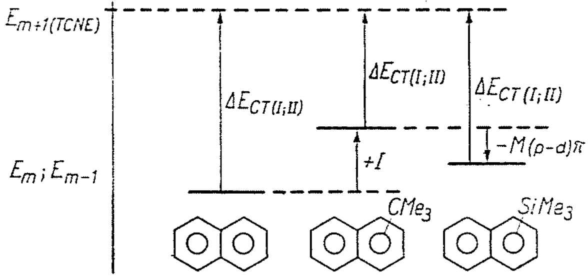

Fig. 3. Illustration of substituent effect on the charge transfer bands of naphthalene derivatives

The results of the study on CT absorption hint to the formation of $(p-d)\pi$ interaction in ground state in accordance with the conclusions drawn by EVANS and al. [7].

The molar absorption coefficients in Table 1 were determined graphically by the use of the BENESI—HILDEBRAND equation (BH equation) [9]. The formation of the donor-acceptor complex, in the case of equimolecular ratio of the components, can be characterized by the following equation:

$$A + D \rightleftharpoons C$$

and the complex stability constant:

$$K_c = \frac{[C]}{([A] - [C])([D] - [C])}$$

In the presence of excess donor:

$$[D] - [C] \simeq [D]$$

[C] can be expressed from the Bouguer—Lambert—Beer formulae, after substitution and transposing the equation for K_c, we get the expression:

$$y = \frac{[TCNE] \cdot l}{\log I_0/I} = \frac{1}{K_c \cdot \varepsilon \cdot [D]} - \frac{1}{\varepsilon},$$

where $\log I_0/I$ is the absorbance

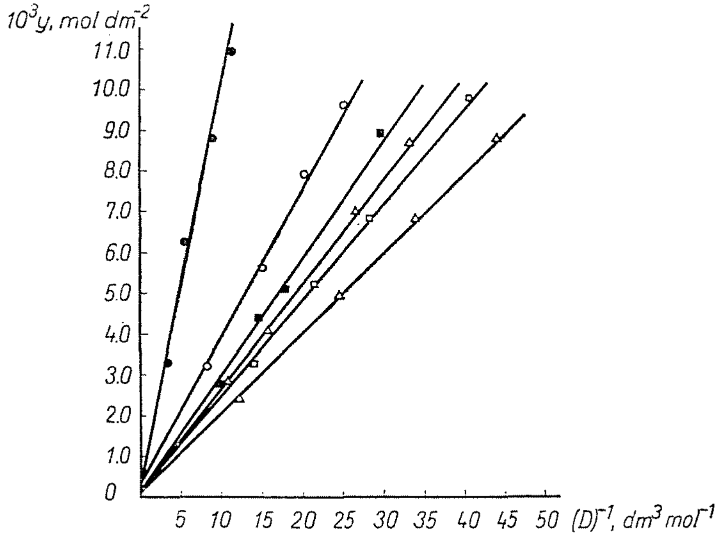

Fig. 4. Graphical evaluation of the CT bands of benzene derivatives on the basis of BH equation; □: trimethylsilylbenzene, ■: tert. butyl-benzene, △: 1-trimethylsilyl-4-methylbenzene, ▲: 1-tert. butyl-4-methylbenzene, ○: 1,4-bis(trimethylsilyl)-benzene, ●: 1,4-bis(tert.butyl)-benzene

ε is the extinction coefficient of the complex, l is the length of the cell used in the spectrophotometric measurements

[D] is the donor concentration

[TCNE] (or [A]) is the acceptor concentration.

In our investigations for benzene compounds the donor concentration was 2—5 times higher than that of the acceptor concentration, for the other compounds the donor concentration was higher at least by an order of magnitude. On the basis of the BH equation the relationship between y and $1/[D]$ was used for the determination of the ε and K_c values of the complexes (Figs. 4—5).

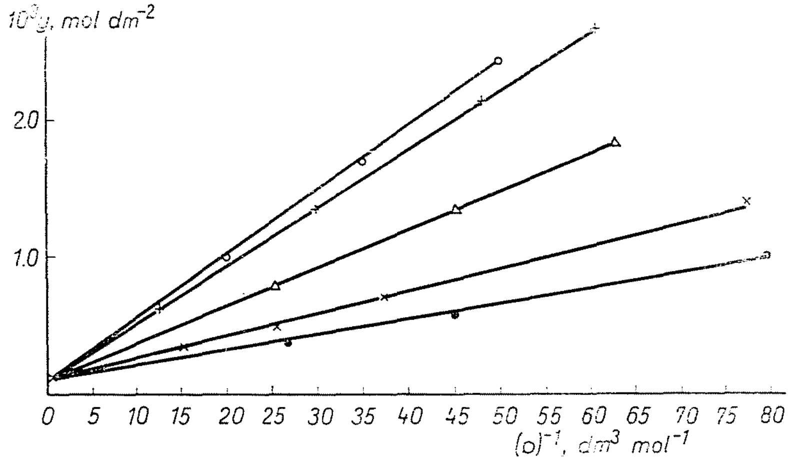

Fig. 5. Graphical evaluation of the CT bands of phenanthrene derivatives on the basis of BH equation; +: phenanthrene, △: 9-trimethylsilylphenanthrene, ▲: 9-tert. butyl-phenanthrene, □: 4,10-bis(trimethylsilyl)-phenanthrene, ■: 4,10-bis(tert.butyl)-phenanthrene

The axial sections of the linear lines in the figures are nearly identical indicating that the intermolecular distance in these complexes can be taken as constant. By the graphical evaluation of the BH equation, 0.2—0.6 l/mol was obtained for the equilibrium constant (stability constant) of benzene derivatives, in agreement with the data in the literature [10].

The extinction coefficients provided for naphthalene derivatives differ markedly from the values given by Evans and al. [7] (Table 1), they show, however, a similar trend. The difference can be attributed to the error of the graphical evaluation method. According to Bendig and al. [11, 12] the determination of K_c by the BH equation is rather inaccurate, since the error made in the determination of ε increases the error in the calculation of K_c. For this reason the complex stability constants have not been included into Table 1. In the case of phenanthrene derivatives the K_c values are in the interval of

3—10 l/mol. The determination of ε and K_c for the anthracene derivatives was impeded by the low intensity of the CT bands, no data related to anthracene compounds are found in the literature.

As it has already been mentioned there is a connection between the ionization potential of the donor and frequency of the charge transfer absorption of lower energy. In accordance with the DEWAR approximation [1, 2], a linear line results from the relation $\tilde{\nu}_{CT} - E_{m(D)}$. The frequencies of the CT I bands are shown in Fig. 6 as a function of the energies for the highest occupied π levels calculated by Hückel's method with ω-technique. The trend of the relationship is clearly seen in the figure. The average of the energy values calculated for organosilicon compounds with two different parameter sets [13] are presented along the abscissa. The quantumchemical calculations overestimate the —M effect of the —SiMe$_3$ group, thus consistently take the —SiMe$_3$ substituted

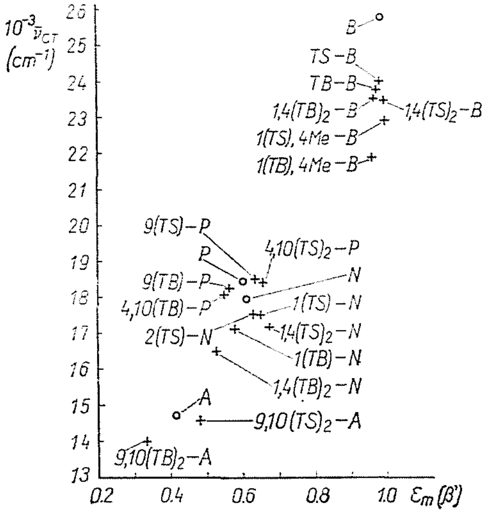

Fig. 6. Relation between the frequency of charge transfer absorption (CT I) and the energy of the highest occupied molecular level (B: benzene, N: naphthalene, P: phenanthrene, A: anthracene, TB: tert. butyl, TS: trimethylsilyl, Me: methyl)

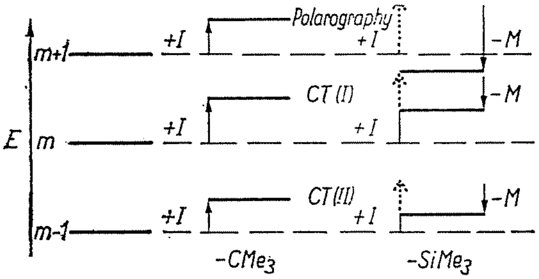

Fig. 7. The effect of substituents on the molecular levels deduced on the basis of results of various experimental methods

compounds more stable than the unsubstituted compounds. The calculated results contradict the experimental findings in the CT spectra according to which the —M effect can only partly compensate the inductive effect of the $-SiMe_3$ group. This contradiction, however, does not mean that the HMO model is inadequate to the interpretation of the experimental results of CT spectra, since the effect of substituents on the energy value of the respective molecular levels can be taken into account by perturbation calculation.

According to BOCK and ALT [10], in the case of $-SiR_3$ substituted aromatic compounds first- and second-order perturbation effects have to be considered. The first-order perturbation includes the change in the coulomb parameter of the substituted carbon atom, the second-order perturbation considers the change of the resonance integral of the C—Si bond, too.

The results of the measurements on the polarographic reduction half-wave potentials [14] for the $-CMe_3$ and $-SiMe_3$ substituted aromatic compounds, the data of UV [15] and CT absorption bands give information on the energy levels of the investigated compounds and may be compared to each other. The experimental results have been summarized in Table 2. All the data are related to the characteristic property of the corresponding unsubstituted compounds as reference material. The p-bands of the UV spectra were approximated (and presented in the last column of the table) as the energy differences of the CT I bands and the polarographic data, and a proper agreement was obtained between the data of the direct measurements and the values calculated from the results of two other experimental methods. All our experimental findings can be summarized as follows:

a) On the basis of polarographic measurements it could be concluded that the energy of the lowest unoccupied π level (LUMO) increases with $-CMe_3$ substitution (+I effect) and decreases in the presence of $-SiMe_3$ group (the +I effect is overcompensated by the —M effect of the group).

b) Investigation of the charge transfer absorption bands indicated that both groups enhance the energy of the highest (and next to highest) occupied π level (the +I effect is dominant), but the effect of the $-SiMe_3$ group is smaller, this refers to the formation of $(p-d)\pi$ interaction in the ground state.

c) The bathochromic shift in the UV spectra of $-SiMe_3$ substituted aromatic compounds in comparison with the spectra of the analogous carbon compounds und unsubstituted compounds supports the assumption on the formation of $(p-d)\pi$ interaction in the excited state. The mentioned bathochromic displacement was also found if the position of the p-band was deduced from the polarographic half-wave potentials and the data of CT bands of the respective complexes (hypsochromic shift was obtained only for the $-CMe_3$ substituted phenanthrene derivatives, this probably might be attributed to the inaccurate assignation of the charge transfer absorption band, since the spectra appeared as the superposition of different CT bands).

Table 2

Comparison of the experimental data of the investigated compounds [in cm^{-1}]

Compound	Molecular levels				
	E_{m-1} (polarography)	E_m CT (I)	E_{m-1} CT (II)	$E_{m+1}-E_m$	
				p-band UV	on the basis of polarography + CT bands
B	0(21000*)	0(26000)	—	0(48360*)	(1360)
TS-B	—	+1640	—	−1150	—
TB-B	—	+2020	—	− 380	—
1(TS),4(Me)-B	—	+2960	—	−3990	—
1(TB),4(Me)-B	—	+4020	—	−1560	—
1,4$(TS)_2$-B	−2130	+2330	—	−3960	−1160
1,4$(TB)_2$-B	—	+2300	—	−1410	—
N	0(15970)	0(18050)	0(23150)	0(36360)	(2340)
1(TS)-N	−325	+540	+160	−900	−2125
1(TB)-N	+480	+870	+270	−1020	−990
2(TS)-N	−80	+480	+470	−260	−1940
1,4$(TS)_2$-N	−1130	+840	+630	−1760	−2630
1,4$(TB)_2$-N	+640	+1470	+630	−1270	−226
P	0(15730)	0(18520)	—	0(34250)	(0)
9(TS)-P	−650	+20	—	−690	−630
9(TB)-P	+240	+200	—	−70	+440
4,10$(TS)_2$-P	−730	+40	—	−130	−690
4,10$(TB)_2$-P	+400	+310	—	−130	+710
A	0(11860)	0(14710)	0(21790)	0(26670)	(100)
9,10$(TS)_2$-A	−2980	+220	+190	−960	−2860
9,10$(TB)_2$-A	−2740	+730	+510	−960	−2210

* Estimated value on the basis of the Streitwieser-Schwager equation (Streitwieser, A., Schwager, J.: J. Phys. Chem. **66**, 2316 (1962)).

Summary

Trimethylsilyl substituted benzene, naphthalene, anthracene and phenathrene derivatives and the analogous carbon compounds were investigated in their molecular complexes with TCNE by CT spectroscopy in dichloromethane solution. The CT absorption band of the organosilicon compounds showed a hypsochromic shift related to the carbon analogues. This experimental fact may be attributed to a $(d-p)\pi$ interaction in the ground state. There is a fair correlation between the energies of the CT bands and those of the highest occupied MO (HOMO) calculated by the HMO method. The molar extinction coefficients and stability constants of the molecular complexes were determined by the Benesi—Hildebrand equation.

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